Exploring homogeneous catalysis for the oxidation of starch

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Chapter 1

The oxidation of starch: benefits, challenges and perspective
1.1 Starch properties

1.1.1 A short history of starch

Processing of starch is one of the oldest technologies in the world, dating back to the Egyptians and possibly even as far back as 10000 years ago.\(^1\)\(^,\)\(^2\) Along with an increase in industrialisation, it became of interest to a large number of chemists and companies worldwide and has seen a huge development both in bulk production and modification from the 1800s and in the subsequent centuries. Starch is used on a million tonnes scale in the bulk chemical, paper and the food industry.\(^3\) Starches are used in the paper industry as surface seizing agents, flocculant, binder and adhesives amongst others.\(^4\) In the food industry, the applications are even wider: sweeteners, gums, fried and baked foods are only a selection.\(^5\) Furthermore, bulk chemicals such as ethanol, polyols or glucose can be produced directly from starch.\(^6\) For most of these applications, native unmodified starch is not suitable. As such, much research has gone into modification of starches and finding the optimal properties for a specific application. Many of these properties depend on the type of starch being used. The main starches used originate from tubers such as potato, cereals such as corn and wheat and roots like cassava.\(^2\)\(^,\)\(^7\) Since these different crops grow in varying conditions, the production of a product from one type of crop is often region dependent. Therefore, companies often focus on one type of crop, which is most abundant in the area. For example, potato grows well in the Netherlands and has been used there as a source of starch since the Middle Ages.\(^2\) Even today, the Netherlands is the 2\(^{nd}\) biggest producer of potato starch in the world.\(^8\) In this work, focus will be mainly on potato starch.

1.1.2 Molecular structure of (potato) starch

The structure of starch, both on a molecular level and on the higher level of the granules (section 1.3, Fig 3), varies greatly between sources. Moreover, the growth conditions (i.e. environment, time of growth) have a large impact on the molecular structure and size of the granules. Still, the main aspects of the structure can be discussed in general terms.

In general, starch is composed of two polysaccharides: amylose and amylopectin. Amylose consists of mainly linear D-glucose units bound via \(\alpha-(1\rightarrow4)\)-glycosidic bonds with an average degree of polymerization (DP) of 900 – 3300 (Fig 1a,b). Within the granule, amylose occurs typically as long amorphous chains in an amount of 17 - 32%. In the presence of complexing agents such as iodine, 1-butanol or fatty acids, amylose will rapidly form single helices. The iodine complexes are the origin of the well-known intense blue colour used in starch-iodine indicators.\(^9\) Besides some minor components such as proteins, lipids, sugars, salts and organic acids, amylopectin is the major component (60 – 80%) of starch. It is also made up of D-glucose units, but is more branched via \(\alpha-(1\rightarrow6)\)-glycosidic linkages along shorter chains linked via \(\alpha-(1\rightarrow4)\)-glycosidic bonds (Fig 1c,d). Amylopectin is mostly crystalline and is
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Figure 1. Molecular structure of amylose (a) and amylopectin (b) with their respective schematic representation showing the linear structure of amylose (c) and branches of amylopectin (d) along with the bonding of the glucose units via $\alpha-(1\rightarrow4)$- and $\alpha-(1\rightarrow6)$-glycosidic bonds.

intersected by long chains of amylose (section 1.3), which will partly co-crystallise into helices. Amylopectin structure varies more significantly than amylose from one crop to the next. A full discussion of the various types of starches is outside the scope of this work and has been reviewed extensively (refs [7,8,10]). The ratio of amylose and amylopectin given here can be tuned to give desired properties by genetic modification. So-called waxy starches were found already at the beginning of the 20th century in China. These starches contain exclusively amylopectin giving interesting properties such as easier digestibility and lower viscosity. Similarly, high-amylose starches were discovered a few decades later by Whistler and Kramer (up to 65% amylose). In later years, the amylose content could be increased to 85%. These are useful to give harder gels and texture to food as well as being interesting for research purposes. 

The overall structure of starch is semi-crystalline, meaning it consists of both crystalline and amorphous lamellae, which can be demonstrated by techniques such as powder X-ray diffraction (XRD) and differential scanning calorimetry (DSC, Fig 2a). This crystallinity arises from double helix formation of amylopectin chains. Short chains of around 12 - 16 glucosyl units form these helices due to strong hydrogen bonding. Amylopectin can crystallise in various ways called A-, B- and C-type allomorphs with slight differences in structure (i.e. unit cell, amount of water in the structure, Fig 3, bottom right). Tubers such as potato, for example, always have B-type crystals. These are characterised by a much higher water content than other allomorphs and loss of water from within these structure will destroy the crystallinity. Because of these
helices, larger structures such as lamellae and blocklets (discussed in section 1.3, Fig 3) will form which eventually make up a granule. The double helices are connected via small linear sections, for this arrangement several models exist which will discussed in

Figure 2. (a) DSC thermograms of barley (- - -) and potato ( ) starch, showing the gelatinization onset (TO), melting (TM) and conclusion (TC) temperatures. The area of the graph from TO to TC is the enthalpy of gelatinization (ΔH), a measure of the amount of crystallization. The arrow shows a second amylose-lipid transition in barley starch. Reproduced with permission from Vamadevan and Bertoft[7], copyright Wiley 2014 (b) Brabender viscoamyllograph traces of several types of starches, indicating the changes in viscosity of starch in water upon heating and cooling. Reproduced with permission from Maurer[4], copyright Elsevier 2009 (c) Changes starch granules in water undergo upon heating, cooling and storage as represented by Goesaert et al.[13] (I) Native granules in water (IIa) Swelling of the granules as the temperature is increased (IIb) When the gelatinisation temperature is reached, the granules will unravel as amylose leaches into the solution and hydrogen bonding between starch chains is disrupted. Eventually, the granule structure is completely destroyed and a starch paste is formed (IIIa) Upon cooling of the starch paste gelation takes place, amylose chains will retrograde to form a network of double helices within several hours (IIIb) During storage of the starch paste amlopectin retrogradation takes places and the amylose network becomes more ordered. Reproduced with permission from Goesaert et al[13], copyright Elsevier 2005.
depth later (section 1.3). Due to the length of amylose chains, they do not form double helices as easily as amylpectin even though it is thermodynamically more favourable. Therefore, in the native granules, amylose is found more in the amorphous regions of the granule while also intersecting crystalline lamellae. After heating and subsequent cooling of native starch in water a process called retrogradation will take place (section 1.4.1). During this process, recrystallization takes place, which causes the amylose chains to form double helices into large ordered structures throughout the solution (Fig 2c). These double helices are much stronger than amylpectin helices. This causes the chains to be less digestible, preventing rapid uptake of glucose in the blood.[7,9,10,12]

1.1.3 Granule architecture

Growth of amylose and amylpectin in starches takes places in such a way that ordered structures called granules are formed (Fig 3). Much research in the past century has gone into analysis of granules to elucidate the exact structure and the role the various components of starch have in this. Even today, some aspects are still unknown due to the complexity of the structure and the difficulties of analysing it within the native granules without alteration of its structure. Analysis of the granule size and surface is relatively straightforward using microscopic tools such as scanning electron microscopy (SEM) or particle size analysis.[10,14,15] Granules are typically in a range of 1 – 100 µm in size, the biggest influence being the growth time of the granules along with the type of starch. The growth time also influences the structure (i.e. length, amount of branching) of amylose and amylpectin. For example, longer growth time allows for longer amylose chains to form. Moreover, chain length also varies along the radius of the granule. Shorter amylose chains are found near the periphery, while longer chains are found near the hilum. Larger granules are typically spherical, although at smaller sizes a variety of shapes is found: e.g. oval (potato), polygonal (corn) and disk-shaped (wheat). On top of shape differences, starch sources show some interesting surface and interior differences. The outside of potato starch granules are mostly smooth and quite resistant to modification (e.g. hydrolysis by acid or enzymes). This has been proposed to be caused by larger blocklets (vide infra) with a higher degree of crystallinity on the periphery of the granules.[16] Other starches such as corn starch can have pores up to 100 nm in diameter which are connected to channels to the hilum. These channels have an impact on modification and digestibility, as enzymes or chemicals can more easily reach the inside of the granules.[7,9,10,12,16]

Within the granule growth rings or shells are present (Fig 3) which in turn are made up of spherical blocklets of 20 – 500 nm (blocklet size is starch type dependent). The presence of blocklets is still debated due to lack of direct evidence, but has become an accepted theory in recent years.[10,16,19,20] Blocklets are build-up of alternating crystalline and amorphous lamellae. The lamellae are mostly amylpectin, both the crystalline and the amorphous, intersected with chains of amylose. Linear chains of amylpectin and
Figure 3. Starch granule organization at various levels as represented by Pérez et al.\textsuperscript{[16]}
At the top left the granule itself is shown, with alternating crystalline and semicrystalline shells and the hilum at the centre from where the granule grows. The shells are made up of blocklets, varying in size depending on the type of shell. One level down can be seen that a blocklet consists of alternating crystalline and amorphous lamellae. The lamellae are build-up of amylopectin and intersected with amylose and lipids. At a molecular level the crystalline helices can form different types of allomorphs (section 1.2). Reproduced with permission from Pérez et al, copyright Elsevier 2009. Redrawn in ref \cite{16} from refs \cite{17,18}.
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Amylose also interact with lipids present in the granules to form single and double helices which give additional strength to the structures (Fig 3, bottom left).[16] Several models have been proposed for the way amylopectin is organised within the semicrystalline growth rings. The cluster model, in which an amylopectin chain penetrates several growth rings and forms clusters of double helices in the crystalline rings (Fig 4).[21] Or the building block backbone model, in which the amylopectin chain which has several clusters of double helices attached runs along a growth ring instead of penetrating several of the rings.[7,9,22,23] Finally, at the molecular level several types of crystallinity are present with varying amounts of water bound via hydrogen bonding to the glucose chains (section 1.2).

Figure 4. Amylopectin organisation within the semicrystalline growth rings as represented by Bertoft.[9] (a) The cluster model in which amylopectin chains (main chains shown in red) penetrate several growth rings and form clusters of crystalline double helices. (b) The building block backbone model in which the amylopectin backbone runs along a growth ring with several double helical structures attached. The grey circles show branches off the main chain, the blue circles show external building blocks where the double helices are connected to the chains. Reproduced with permission from Bertoft,[9] copyright MDPI.

1.1.4 Starch modification
1.1.4.1 Properties of native starch

With insight into the structure of starch on a molecular and granular scale (section 1.2 – 1.3) it is interesting to see how this affects the properties on a macroscopic level. One of the most important properties of starch is how it behaves in water, as most work has been done on suspensions of starch in water. Some work has been done on starch in other solvents such as ionic liquids,[24–26], organic solvent mixtures[27] and supercritical CO$_2$,[28–30] but this is mostly undesirable from an environmental point of view as water is the most abundant and cheap solvent. Even so, starch modification in water is also a challenge as starch is not soluble in water up to approximately 58°C for potato starch (Fig 2a)[7], which is called the gelatinisation onset temperature ($T_o$). Below this temperature,
water will cause reversible swelling of the granule (for a recent review on starch swelling and factors influencing it see ref \[31\]). Due to swelling the size of the granule increases (Fig 2c – I). Above this temperature, a process called gelatinisation takes place at which point the starch granule structure will begin to unravel (Fig 2a/2c – II). The unravelling of the granule is an irreversible endothermic process in which crystallinity is lost due to the loss of hydrogen bonding between the amylose and amylopectin chains. The double helices open up due to hydrogen bonding with water and, at high enough temperature (above \(T_C\)), the starch will be completely dissolved aside from some remnants of the granule (so called granule ghosts). Above \(T_C\), the process is no longer called gelatinisation but pasting and the resulting mixture is a starch paste. To quantify the crystallinity of the granules and get more insight into the gelatinisation process, DSC can be used. This shows the gelatinisation onset temperature and loss of crystallinity through breakage of hydrogen bonding in the main endotherm (peak at \(T_m\), Fig 2a). Large differences between starch types are found and from DSC analysis a lot of information can be gained on the amount and uniformity of crystallinity within a granule.\[7,10,13\]

Starch gelatinisation is a highly complex process which is the subject of much research. The process is influenced by many factors including the type of starch which changes the content of lipids, amylose, proteins and salts and whether the native starch has been modified or not.\[32,33\] Several studies have been performed on the nature and stages of starch gelatinisation, which resulted in various models to better understand and describe the gelatinisation process. One model is that of Donovan,\[34\] which was extended by Jenkins and Donald in 1998.\[35\] This model is a swelling-based model focusing on the analysis of the growth rings by small-angle X-ray scatter (SAXS), wide-angle X-ray scattering (WAXS), small-angle neutron scattering (SANS) and DSC. Upon heating of the granules in excess water they start to swell, taking up more and more water primarily in the amorphous growth rings. This process is reversible below \(T_m\), but at some point the water in the amorphous growth rings will start to affect the amylopectin due to pressure build-up. If the stress of the amorphous sections becomes large enough, the crystalline sections will start to loosen and gelatinise as seen from the main endotherm in DSC (Fig 2a). Goderis et al. recently proposed a modified model to the previously discussed model by Jenkins and Donald in which they deviate on two major points.\[36\] Although they agreed with the swelling-induced granular disruption, they showed by polarised optical microscopy that the swelling and gelatinisation does not occur simultaneously for all granules (as was assumed by most previous studies) but is a concerted process in which granule by granule gelatinises. Additionally, they added the importance of blocklets to the gelatinisation discussion. In fact, the authors discuss that SAXS, which was used in many studies on starch gelatinisation, allows probing the blocklets but not the granules and growth rings as the length scales of the latter two are outside the range of SAXS. Therefore, they do not agree with the conclusions made by previous studies such as disruption of the semi-crystalline growth rings arising due to pressure from the amorphous growth rings. They proposed a variation of the model by studying both corn and potato starch granules. Individual granules
gelatinise rapidly, but not all at the same time, and as soon as blocklets have gelatinised they influence gelatinisation of neighbouring blocklets. For corn starch, a separation of the blocklets before the actual gelatinisation process (at $T_o$) was seen by SAXS which was attributed to the build-up of pressure from the water as the temperature increased. This was made more easy by the pores present in corn granules, which act as weak spots for disruption of the semi-crystalline growth rings. Alternatively, this blocklet separation before $T_o$ was not observed for potato starch as it does not have these pores, but also has long amylose chains which connect multiple blocklets and in this way strengthens them. From these complex models we can see that an in-depth understanding on the gelatinisation process is not easy to achieve, especially when prior modification further changes the interactions within the starch architecture.

After heating of starch in water until a paste is formed, further processes will take place upon cooling, collectively termed retrogradation (Fig 2c – III). Within minutes to hours, the amylose chains which leached out of the granules will start to order into crystalline double helices (Fig 2c – IIIa), driven by the lowering in energy this provides. Large networks throughout the solution will form, causing the paste to form a strong gel. The more amylose was present in the native starch, the stronger the gel will be (i.e. waxy starches will form a soft gel in the absence of amylose). If the solution is stored for longer, the amylopectin chains have time to retrograde as well, while the amylose network becomes tighter and stronger (Fig 2c – IIIb). Retrogradation has a massive impact on the quality of products, mainly in the food industry. In the current food industry, much of the food is required to be kept for a long time, but also withstand various conditions such as freezing and thawing while maintaining taste and form. For example, retrogradation in bread causes staling, making the bread mostly inedible. Retrogradation, but also the expulsion of water upon freezing and thawing due to phase separation (termed syneresis) can cause undesirable changes in frozen foods. Moreover, retrogradation can cause problems in other industries such as the paper manufacturing industry. Therefore, much work has been done in the past century to prevent retrogradation (section 1.4.2 – 1.4.3).[7,10,13]

A way of getting insight into the early stages of retrogradation (Fig 2c – IIIa) is by viscosity measurements using a rapid visco-analyser (RVA) or Brabender (Fig 2b). After $T_o$, the viscosity shows a rapid increase due to leaching of amylose into the solution. After $T_C$ a maximum viscosity is reached followed by a decrease when both amylose and amylopectin dissolve. Then, upon cooling retrogradation can be seen by an increase in viscosity as the chains start to form ordered structures. This increase in viscosity is called the setback. Because amylopectin retrogradation takes place over longer time scales, waxy samples will not show this increase in viscosity in the viscoamylographs (Fig 2b – waxy corn). As such, waxy samples can be suitable for certain applications without further modification which is commercially quite interesting.[7,10,13]

The appearance of a starch paste varies with the type of starch and the modifications done to it. For example, corn starches with a high-amylose content form opaque gels with a lot
of strength due to the formation of amylose double helices.\cite{39} In contrast, potato starch typically forms clear pastes with high viscosity. One explanation for this clarity is the presence of phosphate monoesters, which are found in low amounts (0.04 – 0.09% of starch weight) on amylopectin chains at the 3- and 6-position of the glucose monomers. These anionic groups cause repulsion of the chains, making it harder for them to pack and form highly ordered double helices.\cite{7,40} Phosphorylation of starch has been utilised to give some of these properties to native starches (Fig 5). In doing so, phosphorylated starches have found a range of applications such as thickener, adhesive and surface sizing agent.\cite{41}

### 1.1.4.2 Industrial modification of starch

A large portion of the total starch produced worldwide is modified. The goal of these modifications is to improve upon the properties of native starch (section 1.4.1) which are often lacking in one or way or another, preventing direct application. The amount of modifications possible along with the applications of these modified starches is massive and a full discussion is outside the scope of this work (see refs \cite{4,5,42–45} for a detailed review). For potato starch alone, over 500 different modifications are known.\cite{8} Therefore, several modifications done on an industrial scale will be shortly discussed with some applications.

Many modifications are done via substitution of one of the OH groups. This can

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**Figure 5.** Scheme showing the most common modifications of starch done on industrial scale. All reactions shown are simplified, and only one example of each type of modification is given (see text for more details). Modification at C₆ (see Fig 1) is shown, but modification at C₂ and C₃ will happen and might be preferred in some cases. Hydrolysis mostly takes place at the glycosidic linkages at C₁ and C₄.
be done site selective or on C₂, C₃ and C₆ at the same time. Firstly, acetylation or esterification can be done with two processes most commonly performed: with acetic anhydride (Fig 5, right) or with octenyl succinic anhydride (not shown). Using acetic anhydride, a more hydrophobic starch is obtained, in which the added groups provide steric hindrance to lower crystallisation tendency and thus retrogradation. Similarly to phosphorylated starch, this improves paste clarity and prevents gel formation of the starch paste (section 1.4.1). Etherification has a similar effect, providing an even larger steric effect (Fig 5, top). These substitutions allow the starches to better hold water after freezing and greatly enhance storage stability. As such, they are important in food applications. Moreover, etherified starches are used in the paper industry as coating or surface sizers. Octenyl succinylation gives a starch with emulsifying capabilities.

Substitution with anionic or cationic groups can give starch the capability of sticking to a surface. This gives it excellent properties to be used as adhesive. Negatively or positively charged starches can stick to different surfaces, making both types of modification useful. Advanced adhesives with amphoteric starches (i.e. both anionic and cationic groups in the same starch) have also been produced. Besides phosphorylation, oxidation of starch can give the negative charged starch. Oxidation will be discussed in detail later (vide infra). Several types of cationic starch can be made. Starches with a permanent charge with a quaternary ammonium ion (Fig 5, top left), or with a tertiary amine which require an acidic environment and thus have specific applications. Cationic starches are typically used to provide strength to paper, as thickeners or as flocculating agent.

Cross-linking keeps the granule structure intact and provides it with more strength against processing conditions such as high temperature, acid and shear, typical for food applications. Thus, cross-linked starches improve the quality of the food and allow more intensive processing and longer storage. Common cross-linkers are phosphoryl chloride, sodium trimetaphosphate and adipic acid mixed anhydride. Hydrolysis of starch is done on large scales to break down starch. Stirring of a starch slurry below gelatinisation temperatures in mild acid has been done since the 19th century. The $M_w$ is lowered while keeping the granular structure intact. The viscosity at high temperatures is lowered allowing more starch to be dissolved, ideal for application in moulded gum candy. Enzymatic hydrolysis is done with amylases allowing $M_w$ and viscosity to be set to a specific narrow range, for a desired application (e.g. coating, surface sizer). Control of the pH and temperature during modification, along with removal of the enzyme after reaction can make enzymatic modification more costly than other modification methods. Finally, production of dextrins is done via dry-heating of starch. The hydrolysis decreases the cold-water solubility of the starch and lowers viscosity and amount of gel formation. Applications include coatings for food which provide gloss or barrier properties to oil or sugars.

The modification methods discussed so far are all chemical methods to modify starch. Recently, much attention has been gained for non-chemical methods for modifying
1.2 Oxidation of starch – Application and challenges

1.2.1 Industrial oxidation of starch

The focus will now be changed to the oxidation of starch (Fig 5, bottom left). Starch oxidation has been studied for two centuries and makes up a decent part of the total starch industry, being produced at several billion tonnes per year. Oxidised starch has several properties in common with other modified starches (section 1.4.2). Similarly to phosphorylated, etherified and acetylated starches the carboxylic acid groups provide repulsion between the chains which lower the tendency to crystallise and thus inhibit retrogradation. Therefore the viscosity is stable, meaning it will not change to a large extent after processing, an important property for many applications. The viscoamylograph of the oxidised starch would reflect this by not showing the typical increase in viscosity after cooling along with a lowering in the peak viscosity (i.e. it would be similar to a waxy starch, Fig 2b). Furthermore, oxidised starches have greater paste clarity, are whiter and do not form gels. Retention of water after freezing and thawing is improved along with storage stability compared to native starch. An additional characteristic of the oxidation reaction which is a consequence of the process conditions is that the starch chains will be depolymerised to a certain extent during the oxidation. This lowers the viscosity of the paste and allows more starch to be suspended, improving the processability at larger scales. The main drawback of depolymerisation is that it can lead to large starch losses upon filtration of the oxidised material. Cleaved chains which are too short or are over-oxidised will dissolve and be washed away. Thus the depolymerisation should be limited to an extent which allows high yields.
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Oxidised starch is applied in the paper, textile, laundry and food industries. Application in the textile and laundry industry can be attributed to the increased whiteness of oxidised starch combined with the improved handling due to a lowering in viscosity. The largest amount of starch is used in the paper industry. Again whiteness is an important parameter, and viscosity is even more important as the application of starch to the paper requires the viscosity to be low enough. The anionic carboxylic acid groups allow starch to be used as adhesive for pigments and other types of coatings and as surface sizers. In addition, the food industry applies these starches in gums, coatings (e.g. on fries), bread, frozen foods or for biodegradable packaging.[4,5,8,63]

Oxidation chemistry is quite broad as many different groups can be targeted such as alcohols, amines, sulphides, olefins, aromatics or even alkanes. As such, much research focus has been on obtaining chemoselectivity in the presence of other functional groups. More important for starch oxidation is the selectivity for conversion to carbonyl and carboxylic acid groups and for selectively converting one of the available alcohol groups (e.g. primary vs secondary alcohols).[64] Since the 1800s, oxidation of starch has been done using sodium hypochlorite (NaOCl) and the process has changed relatively little. This can be ascribed to the high efficiency of and control over the process along with the low price of hypochlorite. Hypochlorite can be made on site by diffusion of chlorine into a sodium hydroxide solution. This solution is subsequently added to a starch slurry brought to pH 7 – 11 and stirred at 20 – 40°C for several hours. Due to the formation of HCl during the reaction, the pH will drop requiring addition of base or buffering to maintain constant reaction conditions. Analysis of a desired property such as viscosity during the reaction is often done to determine when the reaction is finished. After the reaction, the pH is brought to 5 – 6 and the excess hypochlorite is destroyed. Finally, the starch is washed and dried. In some cases, yellowing of the starch occurs during the process and some hydrogen peroxide is used as bleaching agent.[62,63]

The mechanism of the oxidation has been studied extensively (Fig 6). A stepwise mechanism is suggested for acid formation in which an alcohol is first oxidised to a carbonyl and subsequently to the carboxylic acid. Due to the various available alcohol groups oxidation occurs at several positions: C2, C3 and C6. Furthermore, oxidative or base-catalysed glycosidic bond cleavage at C1, C4 and C6 (for amylopectin) accounts for the lowering in molecular weight and viscosity observed. Scission of the C2 – C3 bond leads to combined acid and aldehyde (Fig 6b) or dialdehyde formation (not shown) which has a notable effect on the ability to form ordered structure such as double helices. Analysis of the oxidised groups at various pH values suggests the majority of formed carbonyl and carboxyl groups stems from initial cleavage at C2 and C3, indicating a preference for oxidation at these positions.[62]

Many aspects of the reaction are pH, time and temperature dependent. The rate of the reaction is highest at neutral pH and becomes lower as the pH is raised due to the decreased likelihood of anionic hypochlorite to oxidise the alcohol groups. On the other hand, at more alkaline pH, the 2nd oxidation step to the acid is favoured. If an application
requires a high carboxylic acid content ($\text{DS}_{\text{COOH}} = 0.04 - 0.06$, 4 – 6 mol% of oxidised glucosyl units), the reaction will thus be performed at high pH (>11) and the reaction time will be increased. Still, care has to be taken to not have a too long reaction time as this might result in an increased loss of starch because of depolymerisation which is more facile at alkaline pH.\cite{62,63} The amount of carbonyl and carboxyl groups has a direct influence on the properties of the resulting starch.\cite{63} Most of the properties mentioned (\textit{vide supra}) such as paste clarity, viscosity and whiteness will have such a relation to the degree of oxidation. As high carboxyl content provides more repulsion of the chains and decrease crystallisation tendency, clarity and viscosity will improve at higher $\text{DS}_{\text{COOH}}$. Increased whiteness stems mostly from oxidation of coloured impurities. At high levels of carbonyl, yellowing of starch can occur, especially upon heating. Therefore, changing the reaction conditions, and coincidently the degree of oxidation, allows tuning of the properties to the desired level while keeping the loss of starch to a minimum.\cite{62,63}

Not just the mechanism at a molecular level is of interest, much research has gone into the location of hypochlorite oxidation within the granule. Hypochlorite is small and as such can enter the granule easily, providing oxidation throughout the granule while keeping the overall structure intact.\cite{65} The oxidation is not evenly distributed, however, as the crystalline lamellae (Fig 3) are typically difficult to oxidise. This is reflected in the XRD spectra which do not significantly change after oxidation, indicating crystallinity is retained. Accordingly, most oxidation will take place in the amorphous lamellae. Kuakpetoon and Wang found that for high-amylose corn starch the degree of oxidation is quite low and increases upon lowering of the amylose

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{
Likely mechanism for the oxidation of starch by hypochlorite in a neutral or alkaline environment. a) C6 oxidation, b) C2 and C3 oxidation with formation of aldehyde, ketone and carboxylic acid groups. Keto-enol transformations of the formed aldehyde at C2 or C3 occur as well. Note that a stepwise reaction takes place, starting with formation of a carbonyl followed by further oxidation to the acid. Not all glucose moieties will fully oxidise, but stop at the aldehyde or ketone stage. c) C3-oxidation followed by $\beta$-elimination, scission of glycosidic bonds at C4 or C6 (for amylpectin) not shown, but follow similar mechanisms.
\end{figure}
content. Highest DS values were obtained for waxy corn starch. The same group found earlier by studying several types of starch (potato, corn and rice) that the granule shape and type of crystallinity has a large influence on the oxidation reaction.

All in all, much work has been done both industrially and in academia on the oxidation of starch by hypochlorite. However, due to the rise in awareness of the general public as well as of researchers on environmental issues and the problems associated with waste, the process might be seen as problematic. The main issues are the use of stoichiometric oxidant and chlorine with concomitant waste streams. Especially, because the main applications of oxidised starch are consumer products such as paper and food, the use of chlorine is highly undesirable and might face legislative issues in the years to come. For this reason, work on catalytic oxidation of starch has been gaining interest in the last few decades. Catalytic oxidation methods have the potential of remedying the problems with hypochlorite oxidation. Ideal would be the use of oxygen from air as external oxidant, making the process cheap and essentially waste free. Several systems used to oxidise starch will be discussed in the next sections. Finally, the focus will shift to oxidation with oxygen, discussing both systems which have been used to oxidise starch and state of the art systems which have the potential to do so.

1.2.2 Selected catalytic systems for starch oxidation

The challenge in replacing a ubiquitous industrial process such as the hypochlorite oxidation of starch is getting the same properties with a completely different process. The parameters of this reaction have been optimised over decades and as such the product specifications have become narrow. Getting exactly these properties with a new process is thus highly challenging, especially since the interaction hypochlorite has with starch is quite specific. The small size of hypochlorite allows it to easily reach every part of a granule, which might be a problem for large (organometallic) complexes often used in catalytic oxidations. Moreover, catalysts require one or more external oxidants to be re-oxidised, which has an effect on the kinetics of the reaction. The complexity of the system is increased as well, even more so for an already complex system containing the heterogeneous starch chains. Because of this, mechanistic studies are more difficult to perform. Model compound studies might help in this regard, but it is not always easy to translate the results obtained in such a study to starch. On top of this, the depolymerisation of starch, which is so vital for the viscosity of starch solutions, is often not taken into account in these model studies.

Firstly, some processes utilising (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) and derivatives as catalytic oxidant for starch oxidation have been reported (Fig 7). TEMPO is a free nitroxide radical, which is used for a wide range of oxidation reactions. Because TEMPO is the catalytic oxidant, it has to be oxidised back to the active form after oxidising starch which can be done by a variety of oxidants such as oxygen with sodium nitrate, (diacetoxyiodo)benzene, bromine or NaOCl. Most work on starch oxidation with TEMPO has been done in combination with NaOCl as external oxidant. This
Figure 7. Simplified catalytic cycle showing alcohol oxidation with catalytic TEMPO. TEMPO is oxidised with an external oxidant to TEMPO+, which oxidises the alcohol to an aldehyde or ketone (and possibly to the carboxylic acid in a second step). The reduced form TEMPOH can be oxidised to the active species by a two electron pathway or two single electron transfers with loss of a proton. Many different external oxidants have been used to reoxidise TEMPOH. To the right two derivatives of TEMPO substituted at the 4-position with an acetamide- (ACT) or hydroxyl group (4-OH-TEMPO) are shown.

has a significant effect on both regio- and chemo-selectivity. TEMPO mainly converts the C₆ alcohol to aldehydes (Fig 6a). Oxidation to the carboxylic acid is primarily done by NaOCl, although TEMPO can act as oxidant via the geminal diol (formed by hydration of the aldehyde). The tendency to depolymerise starch is much lower than for the conventional process and seems to favour cleavage of the α(1→6) over the α(1→4) linkages. These differences give a modified starch with quite distinct properties from starch oxidised by just NaOCl, making them interesting for specific applications as thickeners or in detergents.[69,70] Moreover, ter Haar et al. found an interesting feature of TEMPO oxidised starches. Due to the positive charge in the active TEMPO⁺ species, it is attracted to the already formed carboxyl acid groups bearing a negative charge. Because of this, oxidation is localised at positions that are already oxidised.[71] Unfortunately, the cost of TEMPO and the necessity for stoichiometric hypochlorite does not solve the problems of NaOCl mentioned previously.

An alternative to the use of a stoichiometric oxidant is the electrochemical regeneration of TEMPO. Electrochemical oxidation of glucose (without TEMPO) has been studied extensively, but has hardly been done on starch. For glucose, a complex process takes place which involves absorption onto a platinum electrode followed by electro-oxidation, formation of an oxygen monolayer onto the electrode and oxidation of the bulk glucose solution. Hernandez-Jaimes et al. found that a solution of gelatinised starch shows similar processes (as seen via oxidation peaks in cyclic voltammograms) but is even more complex due to cleavage of the glycosidic linkages and adsorption of shorter, cleaved chains onto the electrode surface. Furthermore, heterogeneous leftover granule fragments give rise to electrical resistance of the solution. As such, the electrooxidation of starch is difficult to study and very few studies are known.[72] Schnattbaum et al. have reported the TEMPO mediated electrochemical oxidation of starch yielding 63% oxidised starch with a high degree of oxidation (93%). The lack of thorough analysis (only by ¹H and ¹³C NMR) and low yield are not promising, however. The low yield indicates
significant breakdown of the starch, implying favoured depolymerisation pathways.\[73\]

Recently, Rafiee et al. reported the electrochemical oxidation of lignin using 4-acetamido-TEMPO (ACT) as mediator (Fig 7, right). They report a high selectivity for carboxylic acid formation on an extracted lignin. This is interesting as lignin is quite a complex substrate when compared to a typical small molecule. This might make it possible to oxidise starch under similar conditions. Of course, problems with the heterogeneous nature of starch still exist and might make it necessary to work with gelatinised or even cold-water soluble starches to avoid these issues.\[74\]

Replacement of NaOCl seems to be one of the most important features a novel system for starch oxidation should have, since waste generation and use of chlorine is undesirable. One of the most promising candidates in this regard, which is already used and produced on massive scales (4.5 million tonnes per year in 2014)\[75\], is hydrogen peroxide (H\(_2\)O\(_2\)). H\(_2\)O\(_2\) is water soluble, oxidation reactions with it produce primarily water as waste and is highly atom-economical. Some of its primary uses are in wastewater treatment, pulp and textile bleaching and in various chemical reactions such as the epoxidation of propene. Almost all H\(_2\)O\(_2\) (>95%) is produced using the anthraquinone autooxidation process. This process is quite energy intensive, and requires H\(_2\) and air to produce the peroxide. Large amounts of contaminated water is produced and separation of H\(_2\)O\(_2\) from the organic solvent mixture obtained after reaction is challenging.\[75\]

Despite these problems no replacement is available on an industrial scale, although much research is being done into the direct and electrochemical H\(_2\)O\(_2\) synthesis. In the direct synthesis, H\(_2\)O\(_2\) is directly produced from H\(_2\) and O\(_2\). Unfortunately, this only works with pure O\(_2\), which is expensive and poses significant safety risks at the high pressure which is required. Moreover, the yield is quite low due to competing decomposition pathways and extensive purification.\[75-77\] Another alternative, which might overcome some of these problems is the electrochemical synthesis of H\(_2\)O\(_2\) by oxidation of H\(_2\)O or from O\(_2\) and H\(_2\). This has been done on a limited scale so far and requires development of more efficient catalysts. The global focus on renewable energy from wind and solar might make this process more viable as it might be a way to use the electricity surplus generated from these sources at low demand hours.\[76,78\]

In general, catalytic oxidations with H\(_2\)O\(_2\) have the drawback that the catalyst often promotes the decomposition of H\(_2\)O\(_2\) along with the desired reaction. Thus, excess of peroxide has to be added which can be detrimental to the economics of an industrial process. Furthermore, the oxidising nature of H\(_2\)O\(_2\) can cause catalyst decomposition by destroying the ancillary ligand or formation of metal oxides which precipitate from the water mixture (e.g. rust formation in an iron catalysed reaction). A suitable starch oxidation catalyst should thus not only give the desired properties, but be stable under the reaction conditions without catalysing H\(_2\)O\(_2\) degradation to a large extent. Several groups have looked into starch oxidation with H\(_2\)O\(_2\) using metal salts (i.e. CuSO\(_4\), FeSO\(_4\)) as catalysts.\[79-81\] Use of these metal salts in combination with H\(_2\)O\(_2\) is called Fenton chemistry, described first by Fenton in 1894.\[82\] Fenton chemistry is a complex
series of oxidation and reduction reactions, but the most important are the generation of hydroxyl and hydroperoxyl radicals (Fig 8). Hydroxyl radicals are highly reactive and will thus rapidly react with H\textsubscript{2}O\textsubscript{2} to form hydroxyperoxyl radicals and water, requiring a large excess of H\textsubscript{2}O\textsubscript{2} to get a high degree of oxidation of the substrate. On organic substrates, a hydroxyl radical can rapidly abstract a hydrogen atom. α-hydroxyl radicals formed in this way, are rapidly oxidised to the corresponding carbonyl by Fe(III) ions.\cite{83,84} For starch, this results in a high selectivity for carbonyl groups, with only small amounts of COOH formed. Sangseethong \textit{et al.} compared oxidation of a cassava starch suspension by hypochlorite and H\textsubscript{2}O\textsubscript{2} with CuSO\textsubscript{4} (0.1 w\% Cu(II)) as catalyst in alkaline conditions. They found that after 300 min the overall degree of oxidation was similar but the carbonyl and carboxyl contents were reversed, clearly indicating a different selectivity. A similar decrease in hot paste viscosity was observed, attributed to starch depolymerisation, but rheological measurements on both oxidised starches indicated a much higher viscosity due to gel formation upon cooling for the peroxide oxidised starch. The COOH content is clearly an important parameter in determining tendency to form gels. DSC measurements indicated oxidation preferentially took place on amylose, in line with earlier reports.\cite{81} The selectivity for carbonyl formation makes a Fenton process unsuitable for replacement of hypochlorite oxidation of starch. Another major disadvantage of Fenton chemistry is the large amounts of metal salts needed (>0.1 mol\%).\cite{15,81} Even when not taking into account the cost and waste associated with this, Cu ions have been shown to bind to oxidized starch and give colouration to the resulting samples.\cite{85–87} Furthermore, formation and precipitation of significant amounts of metal oxides is likely. For the food industry this has implications for safety, while the textile and paper industries cannot work with a coloured product. Therefore, the use of metal complexes with protective ligands might be a better approach to both allow a lower catalyst loading while also preventing residual metals to contaminate the samples. Sorokin \textit{et al.} attempted to do this using an iron tetrasulfonatophtalocyanine complex (FePcS, Fig 9). They reported that similar degrees of oxidation compared to FeSO\textsubscript{4} could be achieved using this catalyst with 20 times lower loading (0.0078 mol\% and 0.16 mol\%, respectively). The residual iron content at the same time decreased from 190 ppm to an acceptable 20 ppm, close to the iron content in native starch. If 0.0078 mol\% FeSO\textsubscript{4} was used, no oxidation took place, verifying the high activity of FePcS.\cite{15}
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Figure 9. Suggested mechanism for starch oxidation by FePcS (see box) and H₂O₂ at alkaline pH. The oxidant for the initial alcohol oxidation step is unknown, but is expected to be a radical generated by catalysed H₂O₂ decomposition, an Fe(IV)=O species or the nucleophilic Fe(III)-O-O⁻ seen in the 2nd oxidation step. These species can also take part in subsequent COOH formation. These reactions will take place at C₂ and C₃ as well and can lead to depolymerisation at C₁ and C₅ (cf. Fig 6).

The higher activity with higher turnovers suggest a different mechanism operating for this catalyst. Although studying the catalyst during starch oxidation is difficult (vide supra) several studies were done in other systems from which several active species were deduced. Due to the stabilising effect and redox-activity of the PcS ligand, Fe(III)-O-O⁻ and Fe(IV)=O species can be formed (other species such as [Fe(IV)=O]⁺ or Fe(V)=O can be envisioned, but no evidence has been found for them as of yet) which can oxidise starch (Fig 9). The catalyst can subsequently be reoxidised by H₂O₂. Besides these, H₂O₂ degradation still takes place leading to formation of hydroxyl and hydroxyperoxyl radicals, similarly to Fenton systems (cf. Fig 8/9). These species, being similar to those generated in Fenton systems, can oxidise starch in a similar fashion. Which species are most likely to oxidise the alcohol or carbonyl groups in starch requires further study, but might well be a complex mixture of all of them. H₂O₂ decomposition was studied in detail by Tolvanen et al. Without catalyst and starch, at pH = 8.4 and 52 – 55 °C, a linear decrease in H₂O₂ concentration was observed. Decomposition rate was increased by both the addition of starch and catalyst and

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higher catalyst concentrations increased the rate even further.[89] Changes in rate were more striking at different pH values. Near neutral pH lowered the decomposition rate significantly while at pH 10, all H₂O₂ decomposed within a few hours, 5 times faster than at pH 8.4. H₂O₂ decomposition is accompanied by O₂ formation which was formed to a larger extent at higher pH.[90,91] The increase in H₂O₂ decomposition at higher pH indicated increased activity of the catalyst. This was reflected in a change in the degree of substitution, with a notable increase in the carboxylic acid groups. The DS CO was highest at pH 8.4, both DS CO and DS COOH were lower at pH 7.5.[91]

Overall, the degree of oxidation was lower than the values obtained for the oxidation of NaOCl. Moreover, the starch yield of these processes is too low for an industrial process (67 – 95%, lower yields obtained at higher pH). The authors suggest these factors are related to the location of oxidation in the granule. They suspected oxidation mainly takes place on the granule surface (supported by SEM images) and only after extensive breakdown of the surface will oxidation take place within the granule. This breakdown was accompanied by a decrease in starch yield. Low-frequency ultrasound was used in an attempt to increase porosity of the granules and allow oxidation by the catalyst within the granule. Although a moderate increase in DS COOH and yield were observed, the effects were relatively small suggesting a mixing effect leaving the granules mostly unaffected. Most likely, temperature also was a factor in the low yields. 52 – 55 °C is close to the gelatinisation temperature of potato starch (58 °C), making leaching of low molecular weight amylose chains at these temperatures likely, especially under these oxidising conditions.[90,91] Based on these results, using FePcS for industrial oxidation of starch is not viable as the required properties cannot be achieved in combination with low yields. Still, the possibility of catalytic starch oxidation using H₂O₂ was demonstrated making it a good starting point for development of other catalysts for starch oxidation.

### 1.2.3 Catalytic systems for aerobic oxidation of starch

Another oxidizing agent used on an industrial scale is oxygen or air. In principle, air is the most abundant, cleanest and cheapest oxidant.[92] As such, it would be an excellent replacement for hypochlorite oxidation. However, only a few studies of aerobic oxidation of starch have been done. Apart from comparable issues to H₂O₂ (i.e. complexity of a starch suspension making mechanistic studies challenging), O₂ is typically quite unreactive to organic substrates and requires a highly reactive system to be activated.[93] This section will discuss the few reports on aerobic oxidation of starch, followed by a discussion on systems of homogeneous catalysts used for aerobic oxidation of alcohols and aldehydes.

Aside from some early reports on the action of O₂ on gelatinised starch,[94] some of the earliest catalysed aerobic oxidations of suspended starch were by ammonium vanadate (NH₄VO₃). These were reported to introduce more carbonyl functionality than the related industrial reaction, although hardly any carboxyl acid functionality was introduced. Furthermore, the viscosity of the gelatinised oxidised starch was
increased and significant amounts of ammonium vanadate were found in the product resulting in a grey colour.\cite{95,96} Shortly after, Achremowicz et al. reported the CuSO\textsubscript{4} catalysed aerobic oxidation of starch. Analysis of COOH and CO formation were obscured by the presence of Cu carboxylates along with reaction of Cu(II) with the hydroxylamine used in the CO content determination. A lowering in viscosity both in the presence and absence of air suggested changes in the product were mainly due to the addition of the metal salt and not due to a catalytic reaction. Again, the residual metal content in the products was high resulting in colouration.\cite{85} For both of these methods, the large amounts of metal salts required and the difficulties in removing them from the final product makes them unsuitable for the industrial applications.

More recently, Chen et al. reported the use of several heterogeneous isopolyoxovanadates (iPOVs) for the aerobic oxidation of starch.\cite{97} High-amylose (90\%) potato starch was used at a small scale (1.5 g starch) at pH 6 and 50 °C. A high carboxyl content was achieved (DS\textsubscript{COOH} = 1.35 COOH/100 glucosyl units) using Na\textsubscript{4}Co(H\textsubscript{2}O)\textsubscript{6}V\textsubscript{10}O\textsubscript{28}, although with a moderate yield of 86\%. Under these conditions the catalyst could be reused at least 6 times with a moderate drop in the degree of oxidation. When changing the reaction conditions (i.e. pH, time, catalyst amount, T) either the carboxyl content or starch yield dropped rapidly. These factors significantly limit the potential application of this catalyst.\cite{97} All in all, no systems which have the potential to be applicable for the industrial aerobic oxidation of starch have been reported to date.

### 1.3 Scope and outline of this thesis

Starch oxidation is complex due to the architecture of the granule and the intricate way in which it is build-up by amylose and amylopectin. The interactions of starch granules and the industrially used oxidant NaOCl have been investigated in detail, allowing the properties of starch to be tuned by modification to suit a particular application. In spite of the low cost and ease of use of NaOCl as oxidant, it poses burdens on the environment particularly in the form of large volumes of salt waste and chlorinated by-products. Therefore, novel systems which can oxidise starch to meet these same application requirements are needed. Our approach is to look into alternatives such as homogeneous catalysts which have the potential to allow cheap oxidation without the environmental burdens. They should be understood well to allow tuning of their properties or the reaction conditions to reach similar properties to NaOCl oxidised starches.

To this day, the use of homogeneous catalysts for the oxidation of starch have been limited and reports on how starch and the catalysts interact even more so. Work has been done on the use of the environmentally benign H\textsubscript{2}O\textsubscript{2} to oxidise starch in combination with Cu and Fe salts as well as a FePcS complex. Still, these have significant drawbacks such as limited stability of the catalyst, low starch recovery yields and a low degree of oxidation compared to the industrial process. Furthermore, more insight into the interactions of
such a relatively large complex with the starch granule in suspension reactions are required. A novel system for the catalytic oxidation of granular starch has strict requirements (water as solvent, low cost, low T, high turnovers, high stability) making research into a novel system which can handle these demands challenging. This makes it an interesting challenge both from an industrial/commercial perspective due to the cost and toxicity constraints as well as from a fundamental perspective to better understand the interactions of a homogeneous catalyst with the granule architecture. Our focus in this work is on the use of homogeneous catalyst $[^\text{Mn}^{IV}_2(\mu-\text{O})_3(\text{tmtacn})_2][\text{H}_2\text{O}](\text{CH}_3\text{COO})_2$ (Mncat, with tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, Fig 10) and $\text{H}_2\text{O}_2$. Mncat is interesting to study for the oxidation of starch as it is an earth abundant metal, non-toxic catalyst which has been studied for the bleaching of substrates related to starch such as cotton and cellulose. It has been studied both in academia for the oxidation of small molecules (epoxidation, cis-dihydroxylation, oxidation of alcohols and aldehydes), and has been applied industrially in consumer products such as for dishwasher detergents.

In Chapter 2 the catalytic oxidation of potato starch by homogeneous catalyst Mncat and $\text{H}_2\text{O}_2$ is discussed. The influence of various reaction conditions such as $\text{H}_2\text{O}_2$ addition modes, pH, catalyst and oxidant loading on the oxidation efficiency are investigated. This is evaluated by analysis of the degree of oxidation, granular structure and the pasting properties of the starch. The results of catalytic oxidation are compared to oxidation by ubiquitous NaOCl and similarities and differences are discussed. Moreover, the use of Mncat for oxidation of starch in an industrial setting is evaluated.

In Chapter 3 the aim is to better understand the oxidation of potato starch using Mncat, and specifically the manner the catalyst interacts with the granule by performing chemical surface gelatinisation studies. These allow probing of the starch granule at various depths to understand whether oxidation by the relatively large catalytic complex has a preference for oxidation of the granule surface or can oxidise the granule homogeneously. To further investigate this hypothesis, sieving of oxidised starch is performed to probe the degree of oxidation at various granule sizes. The granules are visualised by SEM and light microscopy and further analysed by DSC.

Figure 10. The chemical structure of $[^\text{Mn}^{IV}_2(\mu-\text{O})_3(\text{tmtacn})_2][\text{H}_2\text{O}](\text{CH}_3\text{COO})_2$ (Mncat, with tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane), the main catalyst used in this thesis.
In **Chapter 4** the focus is on the use of **Mncat** and \( \text{H}_2\text{O}_2 \) for the oxidation of 5-hydroxymethylfurfural (HMF). The goal is to use HMF as a model compound to get more insight into the oxidation of starch. Furthermore, a second goal is to perform and understand the oxidation of HMF itself, being a platform chemical of great interest. As such, new selective oxidation reactions with high efficiency catalysts applied to HMF are valuable to study. The oxidation is studied by modification of the reaction parameters to reach a high conversion of HMF as well as to suppress catalyst degradation. Then, the reaction is studied in-depth by means of kinetic and ESI-MS studies to understand the catalytic behaviour and attempt to identify the catalytically active species.

The knowledge gained from the previous chapters is applied in **Chapter 5** to starches of other botanical origins such as corn, tapioca and wheat. Oxidation of these starches with **Mncat** is compared to oxidation of potato starch and differences in oxidation efficiency and final properties amongst the various starches are examined. The influence of variations in granule composition and morphology such as the type of (surface) lipids present, protein content and granule size on the oxidation is evaluated. Then, it is explored whether the thermal properties after oxidation can be linked to the changes taking place on a molecular level.

In recent years the use of pre-treatment by physical or thermal properties in combination with chemical modification of starch has gained attention. In **Chapter 6** pre-treatments such as high-frequency ultrasound (HFUS), ball-milling, blending, ozonation and supercritical carbon dioxide (\( \text{sCO}_2 \)) are used in combination with oxidation by **Mncat** towards potato starches with novel properties. The influence of the pre-treatments on the starch properties are evaluated with or without oxidation and whether there is merit to using these methods in combination with catalytic oxidation both from an industrial and an academic perspective.

In **Chapter 7** oxidation of potato starch by dibasic magnesium hypochlorite (\( \text{Mg(OCl)}_2 \cdot 2\text{Mg(OH)}_2 \), DMH) is researched. The reaction parameters of oxidation with DMH are discussed and the changes in properties it gives to the starch compared to industrially used \( \text{NaOCl} \). Magnesium is of interest primarily for food applications where it can help to limit the drawbacks of magnesium deficiency which are a growing problem due to the consumption of processed foods. Thus, the amount of magnesium incorporated in the starch after oxidation is analysed as well as the ways it modified the starch properties.


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